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PHOTOREACTION OF AROMATIC KETONES WITH ETHYLALUMINUM DICHLORIDE

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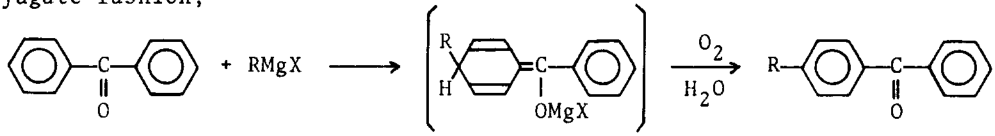
While aromatic ketones as well as aliphatic ketones are known to react with trialkyl- or triarylaluminums to give addition and/or reduction products, monoalkylaluminum halides do not react with them under normal conditions.1) We have found the conjugate addition of ethylaluminum dichloride ($EtAlCl_2$) toward simple aromatic ketones upon irradiation. The conjugate addition of organometallic compounds to aromatic ketones had not been observed except sterically hindered ketones like mesitylphenyl ketone,2) until Holm recently reported that secondary and tertiary alkyl Grignard reagents can in fact add to benzophenone itself in a conjugate fashion;3)



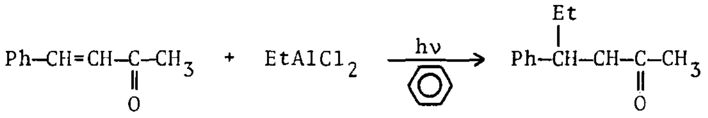
(R: Secondary or tertiary alkyl.)

However, complete lack of the conjugate addition has also been noticed for primary alkyl Grignard reagents.3b)

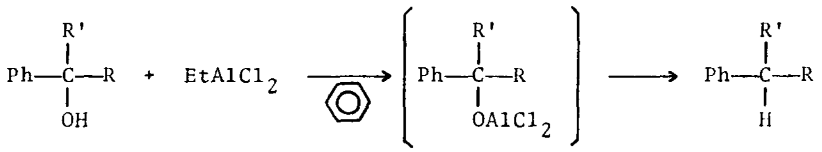
Photolysis of a solution (0.70 M) of an equimolar mixture of acetophenone and $EtAlCl_2$ in dry benzene with a 300 W high-pressure mercury lamp with quartz housing under an atmosphere of nitrogen for 40 hr at room temperature gave after hydrolysis, *o*-ethylacetophenone (14 %), *p*-ethylacetophenone (26 %), ethylbenzene (4 %), and *sec*-butylbenzene (7 %), together with the recovered ketone (55 %). A similar irradiation of benzophenone yielded *o*-ethylbenzophenone (12 %), *p*-

ethylbenzophenone (28 %), diphenylmethane (15 %), and 1,1-diphenylpropane (5 %). On heating at 80°C without irradiation a large amount of benzophenone was recovered unchanged, accompanied by trace amounts of diphenylmethane and 1,1-diphenylpropane.

The reactions of phenylbenzyl ketone and dibenzyl ketone indicated that the conjugation of a carbonyl group with a phenyl ring is essential for this aromatic alkylation. Ethylation of phenylbenzyl ketone occurred only at the ring directly linked to the carbonyl group. This is in contrast to the alkylation of the ketone with the Friedel-Crafts reagent ($EtBr—AlCl_3$) where only the phenyl group separated from the carbonyl group by the methylene group is slowly alkylated. Dibenzyl ketone was recovered almost unchanged from the reaction mixture without yielding any ring-alkylated product. Benzalacetophenone reacted with $EtAlCl_2$ upon irradiation to give a 1,4-addition product (30 %);

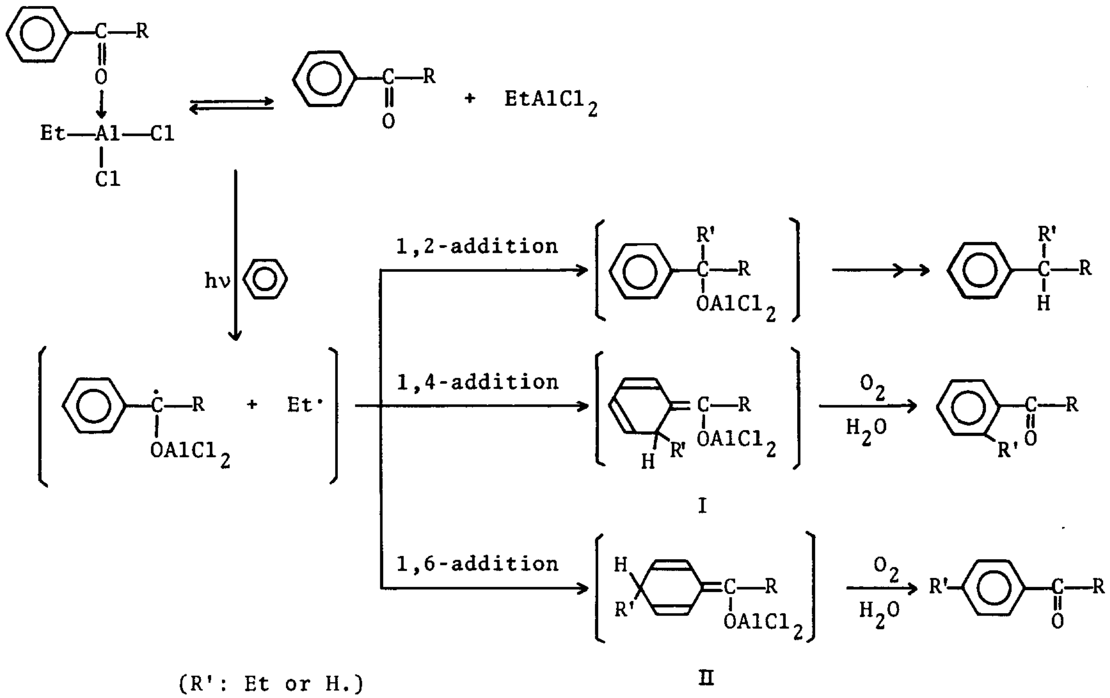


Although normal 1,2-addition or reduction products are also expected, neither 1,1-diphenylpropanol nor benzhydrol in case of benzophenone was detected. Instead, the formation of the corresponding hydrocarbons, 1,1-diphenylpropane and diphenylmethane, was observed. Acetophenone gave a similar result. It was assumed that the 1,2-addition products, dichloroaluminum alcoholates, may be unstable and decompose to the products including the corresponding alkanes.[4] In fact, these benzylic alcoholates prepared in situ from the corresponding alcohols and $EtAlCl_2$ were found to be rapidly converted to the alkanes in moderate yields;



(R: Me or Ph. R': H or Et.)

The reaction may be outlined as follows;



(R': Et or H.)

Although information about the initial photoprocesses of the reaction is lacking, the reaction of the triplet ketones with $EtAlCl_2$ to produce the aluminum ketyl and ethyl radicals may be presumably involved. Formation of similar radicals has been proposed in the Grignard reaction of aromatic ketones resulting in the conjugate addition.3) Trialkylborane has been reported to react with triplet ketones to yield alkyl radicals.5) The process leading to the final products from the conjugate addition products, I or II, may involve air oxidation of them during hydrolysis in an analogous way observed in the aromatic substitution with Grignard reagents.2,3)

The ring alkylation did not occur at appreciable rate when benzonitrile or methylbenzoate was irradiated with $EtAlCl_2$.

References

1) H. Reinheckel, Organometal. Chem. Rev. A., 4, 47 (1969); S. Pasynkiewicz and

E. Sliwa, J. Organometal. Chem., 3, 121 (1965).

2) R. Gaertner, Chem. Rev., 45, 493 (1949); R. C. Fuson, "Organometallic Chemistry," Vol. I, edited by F. G. A. Stone and R. West, Academic Press, New York (1964), p. 221.

3a) T. Holm and I. Crossland, Acta Chem. Scand., 25, 59 (1971);

b) T. Holm, J. Organometal. Chem., 29, C 45 (1971);

c) Cf. C. Blomberg, ibid., 45, 52 (1972).

4) Cf. C. Harris, T. Mole and F. D. Looney, Tetrahedron Letters, 4195 (1966); A. Meisters and T. Mole, Chem. Comm., 595 (1972).

5a) M. V. Encica and E. A. Lissi, J. Organometal Chem., 29, 21 (1971);

b) A. G. Davies, B. P. Roberts and J. C. Scaiano, J. Chem. Soc. (B), 2171 (1971);

c) A. G. Davies and J. S. Scaiano, J. Chem. Soc., Perkin Trans. II, 2234 (1972).